

Appendix G

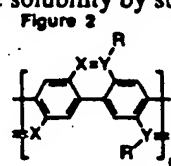
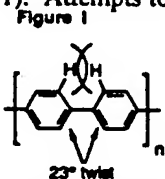
SYNTHESIS OF PLANAR POLY(*p*-PHENYLENE) DERIVATIVES FOR MAXIMIZATION OF EXTENDED π -CONJUGATION

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Abstract: Described is the synthesis of a ladder polymer with a poly(*p*-phenylene) (PPP) backbone. The main PPP backbone was synthesized via palladium-catalyzed coupling of an arylbis(boronic ester) with an aryl dibromide. Imine bridges, formed by exposure of the polymer to trifluoroacetic acid, are used to force the consecutive units into planarity. The bridging units are sp^2 hybridized thus allowing for greater π -electron flow between the consecutive phenyl units by lowering the band gap between the hydroquinoidal and the quinoidal forms of the phenylene backbone. When the bridges are *n*-dodecyl substituted, the fully planar structures (with $M_n < 5\,000$) are soluble in hot chlorobenzene from which flexible free standing films can be cast. The *n*-butyl substituted polymers and the higher molecular weight *n*-dodecyl substituted polymers are soluble in CH_2Cl_2 /trifluoroacetic acid mixtures. The optical spectra of the planar systems are compared to that of the parent nonplanarized polymers, some analogous planar oligomers, and oligo(*p*-phenylenes).

INTRODUCTION

Poly(*p*-phenylene) (PPP),¹ a highly insoluble polymer that has been studied extensively for its possible electronic and photonic applications, has a 23° twist^{1c,2} between the consecutive aryl units due to ortho hydrogen interactions (Fig 1). Attempts to enhance the solubility by substitution of the

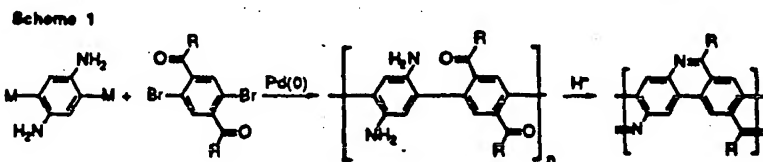


rings forces the consecutive aryl units even further out of plane resulting in a plummet of the extended conjugation (easily observed by the optical spectra).^{1i-k} Here we describe a synthetic route to ladder³ PPP derivatives with bridges that (1) form in high yields upon protonic activation once the PPP backbone is intact, (2) can be substituted so that the newly formed polymer is soluble and processable, unlike many other aromatic ladder

polymers, and (3) contain a double-bonded unit to keep the consecutive aryl units planar while maximizing extended π -conjugation through the PPP backbone thereby increasing the band width (lowering the band gap) between the hydroquinoidal and quinoidal forms (Fig 2).^{1c}

RESULTS AND DISCUSSION

In order to accomplish the required synthesis, we proposed to use the efficient palladium-catalyzed cross coupling reaction of arylmetals with aryl halides to form the initial phenylene portion of the backbone. Acknowledging that introducing functionalities onto the rigid-rod polymer backbones in high yields would be extremely difficult with current synthetic architectural methodologies, we sought to have all the bridging atoms and the solubilizing substituents in place within the monomers prior to the initial aryl-aryl cross coupling reaction. The approach involved formation of an imine bridge between the newly formed consecutive aryl units where the carbon atom in the imine bridge would bear the needed long-chain solubilizing substituent without obstructing the cross coupling reaction (Scheme 1, M = metal). Moreover, imine formation would be nearly

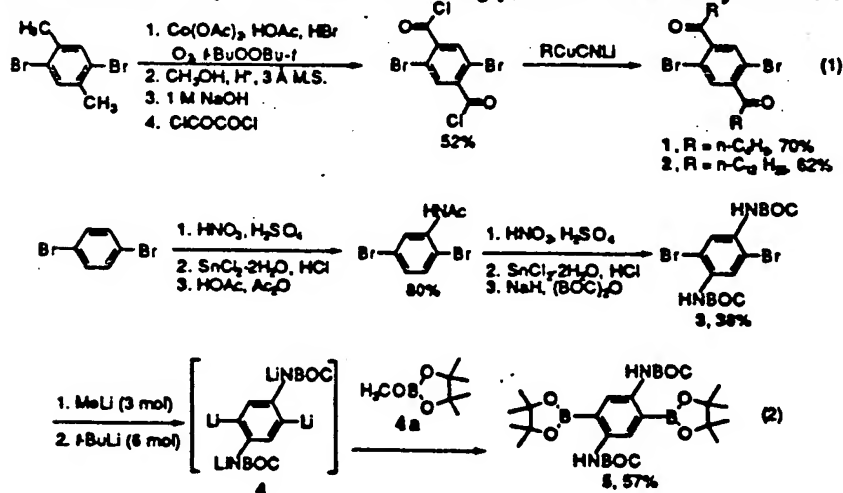


quantitative upon protonic activation and imines possess the π -bond needed to enhance the extended π -conjugation between the consecutive phenylene units. The additional beauty of this approach is that if solubility of the planar system did turn out to be a problem, one could cast films of the pre-cyclized material, introduce an acid catalyst, and promote the imine formation (cyclization) on the intact films. We also chose to keep the halides on the partner since oxidative addition with palladium(0) catalysts is facilitated by electron withdrawing groups on the ring and retarded by electron donating groups such as amines.

We then embarked on several model studies to make imine-bridged phenylene dimers and trimers. Several requirements became obvious. First, the cross coupling reactions were far more efficient with boric acids and

esters than with trialkylstannanes as the metal-containing aryl partner. Though Grignard and zinc reagents have been utilized with great success in cross coupling reactions, our need to purify the intermediates for obtention of 99.9+% pure monomers for the step growth polymerization was paramount. The more electropositive metals like magnesium and zinc do not permit simple chromatographic purification due to rapid protonation of the arylmetal intermediates. Secondly, though the boronic acids can be purified and cross coupled in very high yields, the bis(boronic) acids (i.e. where $M = B(OH)_2$ in Scheme 1) were very difficult to produce in the required purities needed for the step growth polymerization. Hence we chose to use the bis(boronic) esters as a suitable alternative. We eventually converged on several nearly quantitative model reactions using tetrakis(triphenylphosphine)palladium(0) catalysis in alkaline 1,2-dimethoxyethane (DME) for the cross coupling followed by protonic removal of a *tert*-butoxycarbonyl (BOC) protected amine with concomitant imine bridge formation.

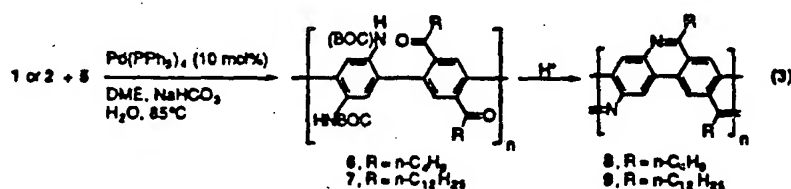
We then synthesized two key monomers needed for the desired planar ladder polymers (eqs 1 and 2).^{4,5} Interestingly, while 3 was nearly insoluble



in diethyl ether, it could be tetralithiated in ether to form a soluble intermediate 4 in almost quantitative yield (checked by addition of chlorotrimethylsilane and isolation of the arylbis(silane) after aqueous work-

up). Treatment of 4 with methyl pinacol borate 4a afforded the crystalline monomer 5,6

Reaction of 1 or 2 with 5 yielded the soluble polymers 6 and 7, respectively, from which size-exclusion chromatography (SEC) could be used to determine the hydrodynamic volumes relative to polystyrene (6: 45% yield after fractional precipitation, $M_n = 6180$ with $M_w/M_n = 2.32$; 7: 73-78% yield after fractional precipitation, $M_n = 4370$ -13280 with $M_w/M_n = 1.78$ -2.60). Upon exposure of 6 or 7 to trifluoroacetic acid (TFA), quantitative loss of the BOC protecting group and cyclization afforded 8 and 9,

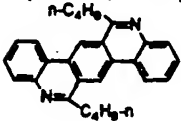
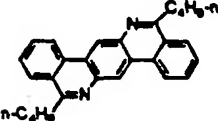


respectively (eq 3).⁷ 9 (from samples with $M_n < 5000$ for the uncyclized precursor 7) can be dissolved in hot chlorobenzene and cast into flexible free-standing films. The dodecyl groups are apparently exerting a plasticizing effect so that the planar rigid-rod polymer can be made to exhibit good film-forming properties. 8 and higher molecular weight samples of 9 can be solubilized with $\text{CH}_2\text{Cl}_2/\text{TFA}$ mixtures.

Powder X-ray diffraction (XRD) of the unannealed 8 and 9 showed a broad pattern approximately 3.4 and 4.7 Å, respectively (weak and possibly characteristic of the π -stacking distance), and strong sharp peaks at 15.4 and 29.9 Å, respectively, characteristic of a smectic glass-like order. Differential scanning calorimetry (DSC) (50-350°C, 20°C/min, N_2) of 9 ($M_n = 4370$, $M_w/M_n = 1.87$) showed a single exotherm at 200°C on the first run while the DSC curve was featureless on the second run. Thermogravimetry (TG) (50-900°C, 20°C/min, N_2) of 9 ($M_n = 4370$, $M_w/M_n = 1.87$) showed no weight loss up to 240°C, 10% weight loss at 440°C, and 62% weight loss at 900°C. Most interesting is the optical absorption data showing enormous bathochromic shifts in the polymer upon cyclization (conversion of 6 to 8 and 7 to 9) (Table I). The absorbances of these planar polymers are far greater than those of oligo(*p*-phenylenes) or PPP.

Thus we succeeded in greatly increasing the extended π -conjugation of PPP derivatives while maintaining a soluble polymeric material. Further methods to enhance the extended π -conjugation in related aromatic structures are currently under investigation.

Table I

Compound (M_n : M_w/M_n)	Absorbance (CH_2Cl_2) (nm) ^a
6 (6 180; 2.32)	<u>250</u> , 320 (sh)
7 (4 370; 1.87)	<u>250</u> , 314 (sh)
7 (13 280; 2.60)	<u>250</u> , 308(sh), 364 (sh)
	<u>300</u> (ref 8)
	<u>294</u> (ref 8)
8 (6 180; 2.32) ^c	374 (sh), <u>396</u> , 425 (sh), 514, 555 (ed) ^d
9 (4 370; 1.87) ^c	<u>392</u> , 488, 525 (ed) ^d
9 (13 280; 2.60) ^c	376 (sh), <u>400</u> , 428 (sh), 516, 560 (ed) ^d
p-heptiphenylene	<u>323</u> (ref 9)
PPP (calcd infinite M_n)	<u>344</u> (ref 9)

^a λ_{max} is underlined, (sh) is shoulder, (ed) is tailing edge at approximately 10% of λ_{max} intensity. ^bAlso a strong carbonyl absorbance at 196 nm. ^cThese molecular weights and polydispersities are from the uncyclized precursors. ^dRecorded in a mixture of CH_2Cl_2 and trifluoroacetic acid.

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